Lawrence Livermore National Laboratory

Chemical Kinetic Models for Advanced Engine Combustion

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Lawrence Livermore National Laboratory
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DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation

Washington, DC

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LLNL-PRES-729740

Overview

Timeline

- Project provides fundamental research to support DOE/ industry Advanced Engine Combustion projects
- Funded by 3-year Lab Call starting FY17

Budget

Project funded by DOE/VTO:

- FY16: 532K
- FY17: 532K

Barriers

- Increases in engine efficiency and decreases in engine emissions are being inhibited by an inadequate ability to accurately simulate in-cylinder combustion and emission formation processes
  - Chemical kinetic models for fuels are a critical part of engine simulation models

Partners

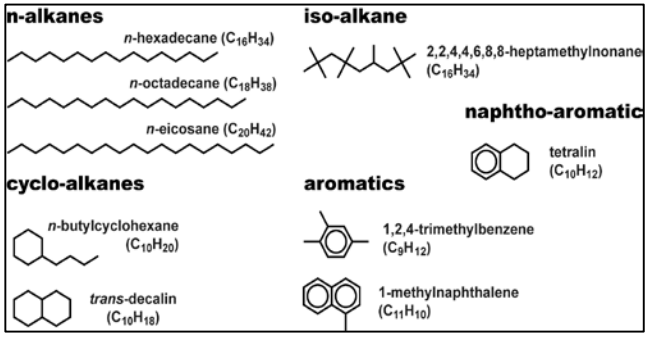
- Project Lead: LLNL – W. J. Pitz (PI)
- Part of Advanced Engine Combustion (AEC) working group:
- – 15 Industrial partners: auto, engine & energy
- – 5 National Labs & 11 Universities
- UConn: RCM data on diesel surrogate mixtures
- Sandia: Provides engine data for validation of detailed chemical kinetic mechanisms
- AVFL-18a working group of the Coordinating Research Council (CRC)

Objectives and relevance to DOE objectives

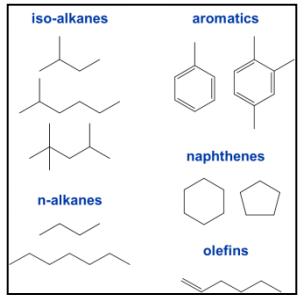
- Objectives:
  - Develop predictive chemical kinetic models for gasoline, diesel and next generation fuels so that simulations can be used to overcome technical barriers to advanced combustion regimes in engines and needed gains in engine efficiency and reductions in pollutant emissions

- FY17 Objectives:
  - Develop a kinetic model for all the nine components on the CRC AVFL-18 diesel surrogate palette
  - Validate & improve diesel surrogate fuel component and mixture models using experimental data from UCONN's RCM
  - Improve chemical kinetic models for components and their mixtures in gasoline using new RCM data from ANL and NUIG

CRC AVFL-18 Diesel surrogate palette:

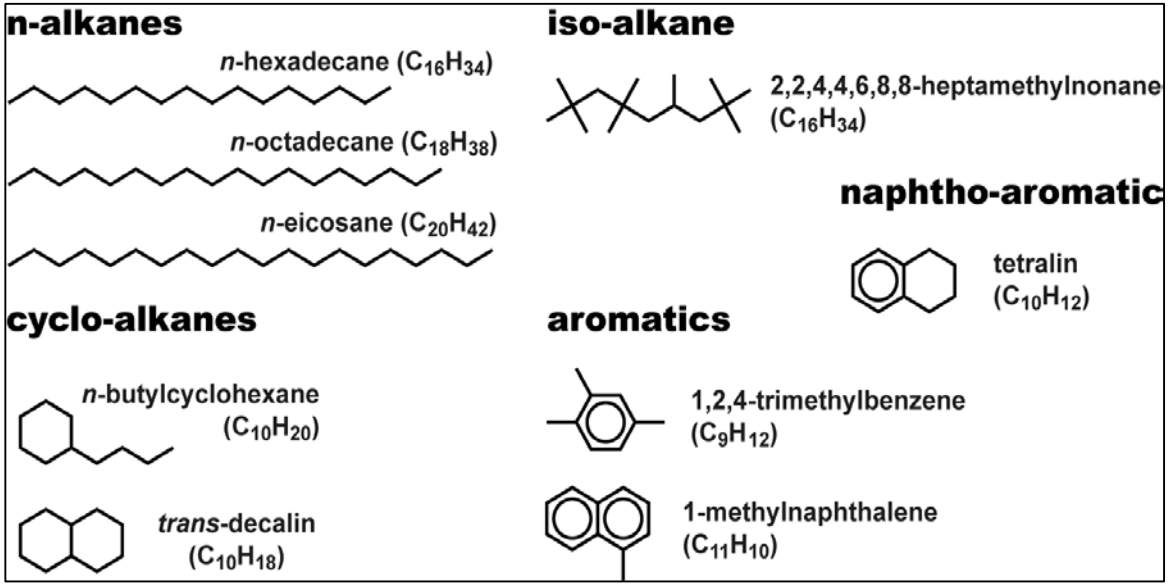


10-component gasoline surrogate palette:



Chemical kinetic milestones

- ✓ Develop preliminary diesel surrogate mixture model including all fuel components in AVFL18 9-component diesel surrogate palette.(December, 2016)



CRC AVFL-18 Diesel Surrogate palette[1]

[1] Coordinating Research Council (CRC) AVFL-18 Working Group. Mueller, C. J., Cannella, W. J., Bruno, T. J., Bunting, B., Dettman, H. D., Franz, J. A., Huber, M. L., Natarajan, M., Pitz, W. J., Ratcliff, M. A. and Wright, K., Energy & Fuels 26(6):3284–3303 (2012).

Approach

- Develop surrogate fuel models for gasoline, diesel, and next-generation fuels to enable the prediction of the effect of fuel properties on advanced engine combustion

- Develop chemical kinetic reaction models for each individual fuel component of importance for surrogate fuels for gasoline, diesel, and next generation fuels

- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels
  - diesel fuel
  - gasoline (advanced compression ignition and/or DISI engines)
  - addition of ethanol and other blendstocks

- Reduce mechanisms for use in CFD engine simulation codes to improve the capability to simulate in-cylinder combustion and emission formation/destruction processes in engines

- Use the resulting models to simulate practical applications in engines, including diesel, advanced compression ignition and DISI, as needed

- Iteratively improve kinetic models as needed for applications
- Make kinetic models available to industry

- Addresses barriers to increased engine efficiency and decreased emissions by allowing optimization of fuels with advanced engine combustion

Technical Accomplishments: Kinetic model of the CRC diesel surrogate palette assembled with preliminary validation!

Components selected from the CRC AVFL-18 Diesel Surrogate palette[1]:

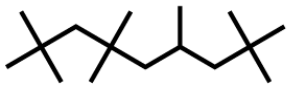
n-alkanes

n-hexadecane ($C_{16}H_{34}$)

n-octadecane ($C_{18}H_{38}$)

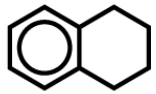
n-eicosane ($C_{20}H_{42}$)

iso-alkane



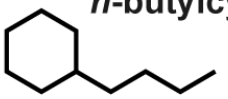
2,2,4,4,6,8,8-heptamethylnonane ($C_{16}H_{34}$)

naphtho-aromatic

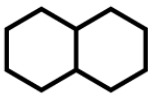


tetralin ($C_{10}H_{12}$)

cyclo-alkanes

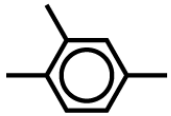


n-butylcyclohexane ($C_{10}H_{20}$)

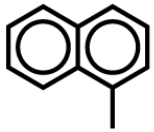


trans-decalin ($C_{10}H_{18}$)

1- & 2-ring aromatics



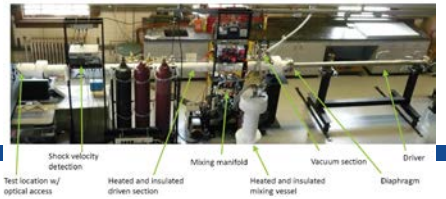
1,2,4-trimethylbenzene (C_9H_{12})

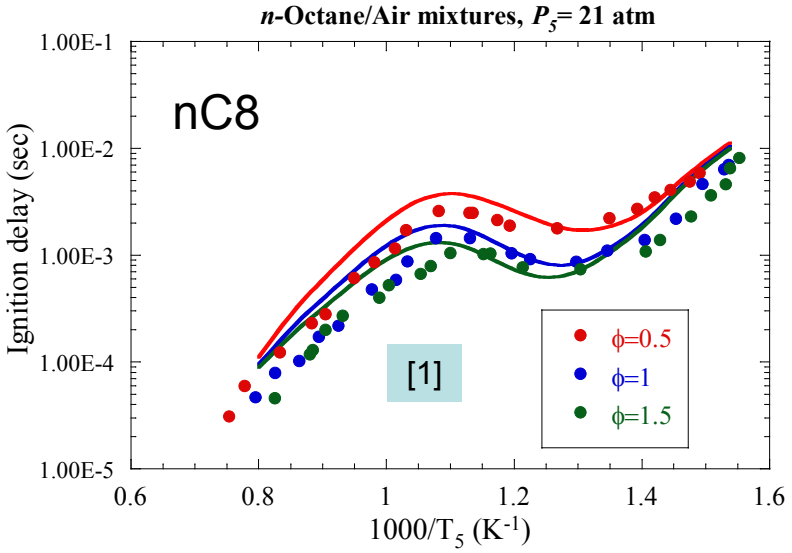


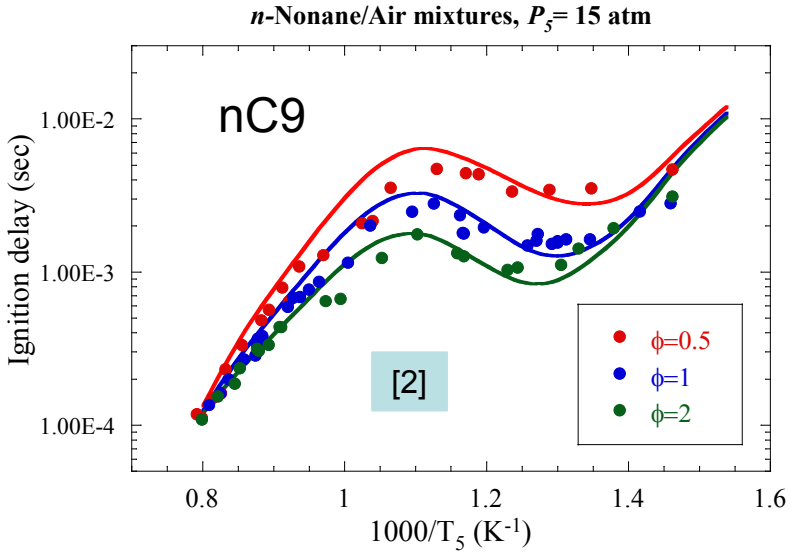
1-methylnaphthalene ($C_{11}H_{10}$)

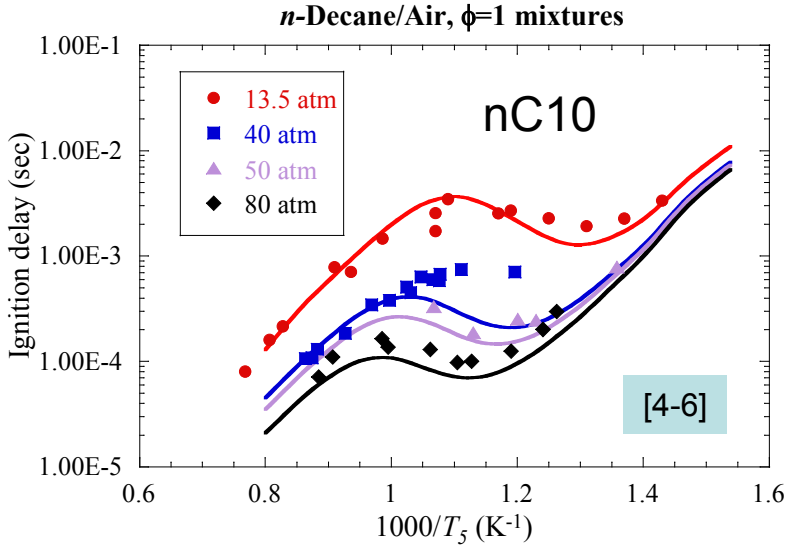
[1] Coordinating Research Council (CRC) AVFL-18 Working Group. Mueller, C. J., Cannella, W. J., Bruno, T. J., Bunting, B., Dettman, H. D., Franz, J. A., Huber, M. L., Natarajan, M., Pitz, W. J., Ratcliff, M. A. and Wright, K., Energy & Fuels 26(6):3284–3303 (2012).

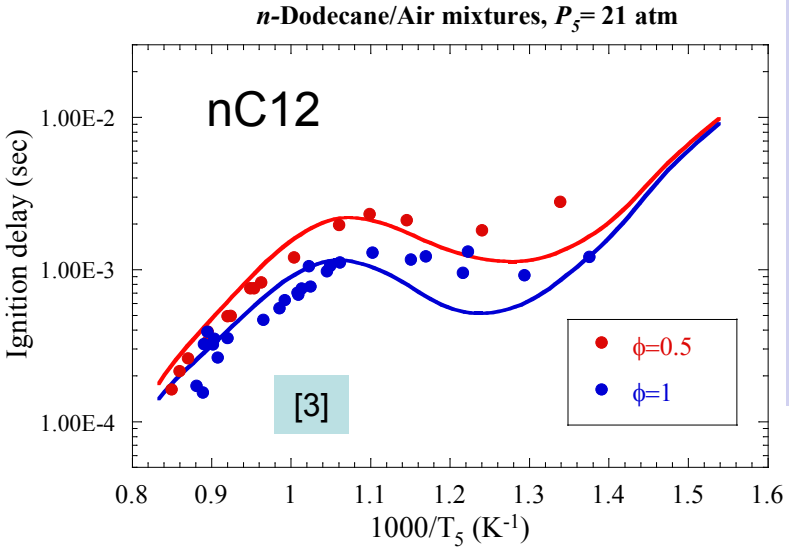
Large n-alkane kinetic models improved





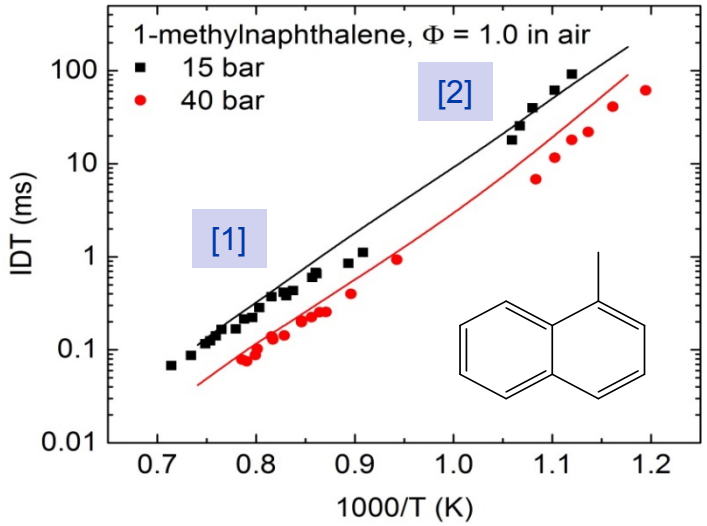


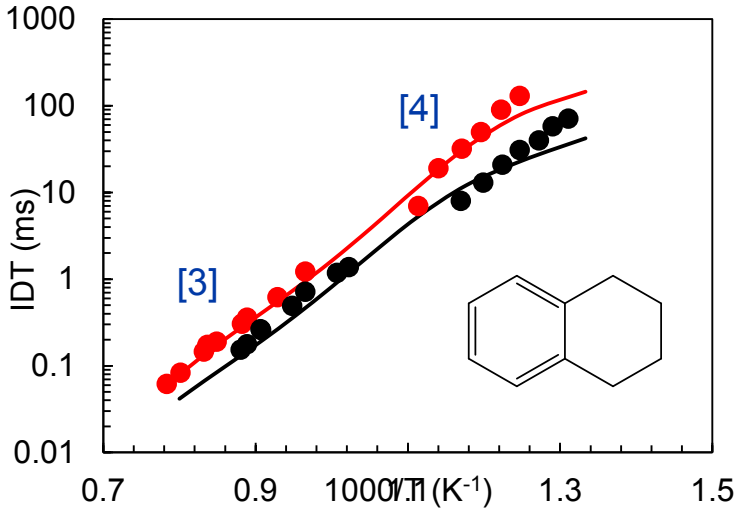




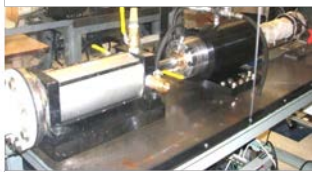
[1] Sarathy et al. Combust. Flame 158 (2011), 2338-2357
[2] Yong et al., Fuel, 188 (2017), 567-574
[3] Vasu et al. Proc. Combust. Inst. 32 (2009), 173-180
[4] Pfahl et al. , PROCI, 26 (1996), 781-789
[5] Shen et al. ., Energy and Fuels, 23 (2009), 2482-2489
[6] Zhukov et al. CNF, 153 (2008), 130-136a

1-methylnaphthalene, tetralin and decalin kinetic models improved

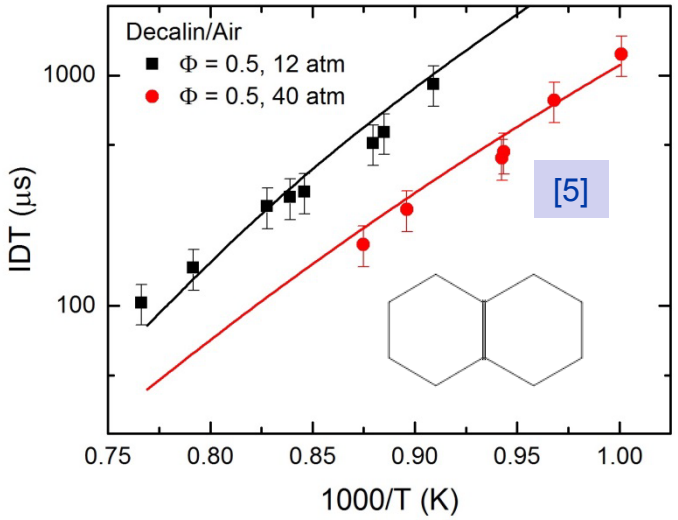




[RPI Shock tube](#)



[UConn RCM](#)



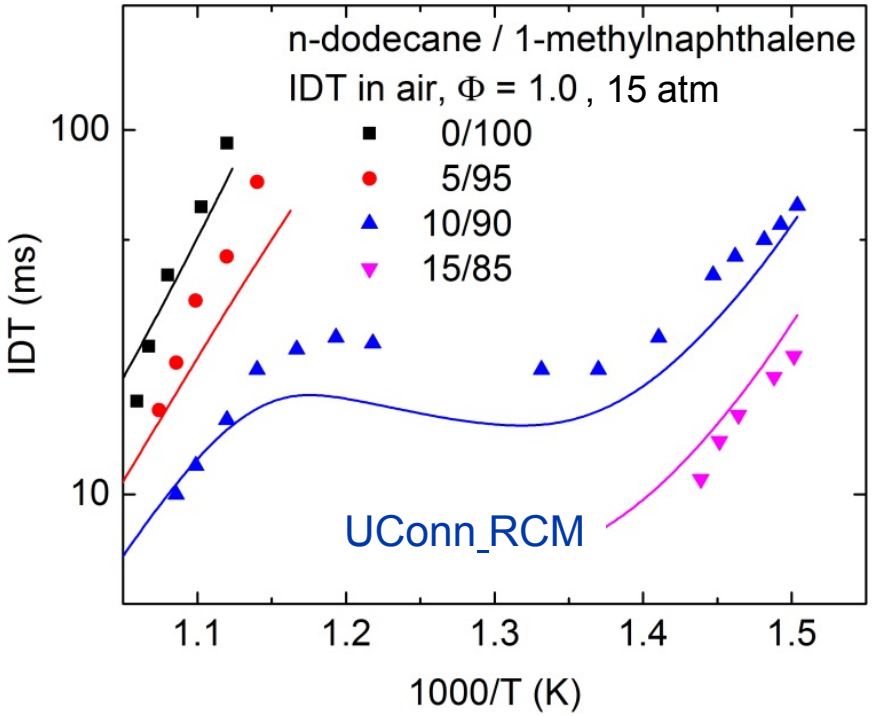
[1] Wang et al. , Combust. Flame 157 (2009), 1976-1988
[2] Kukkadapu et al, Energy and Fuels, 31 (2017), 854-866.
[3] Wang et al. Energy and Fuels, 27 (2013), 5483-5487
[4] Kukkadapu et al., Fuel, 159 (2015), 436-445
[5] Oehlschlaeger et al., Energy Fuels 23 (2009) , 1464–1472

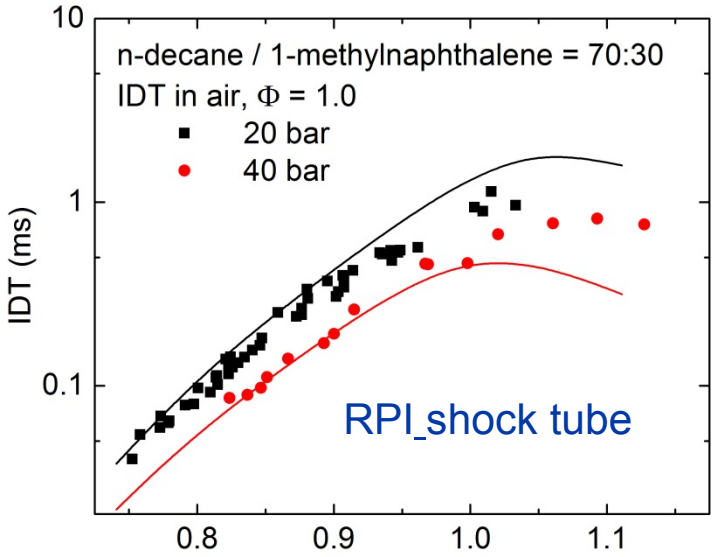
New decalin experimental data measured at UCONN (Sub-contracted by LLNL)

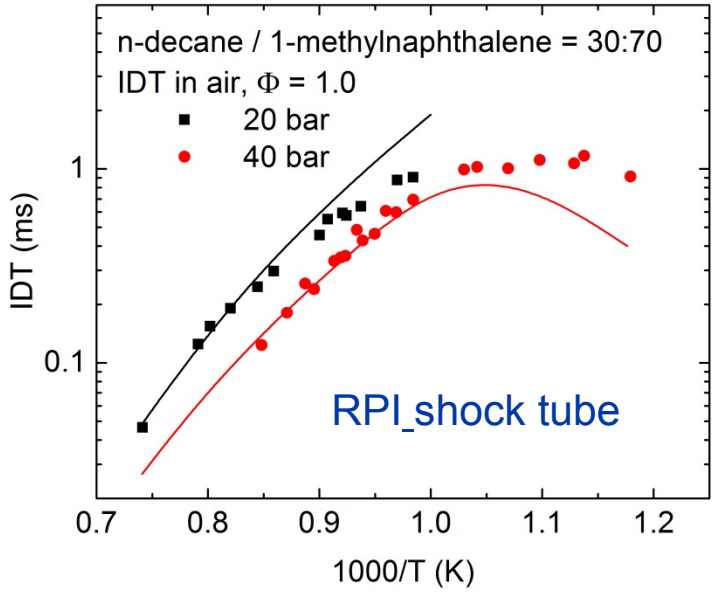
Blend behavior in kinetic model improved: n-decane or n-dodecane with 1-methylnaphthalene

The agreement between experimental and simulated results for blends indicate good consistency between component submodels

Kukkadapu et al, Combust. Flame, (2017), under review

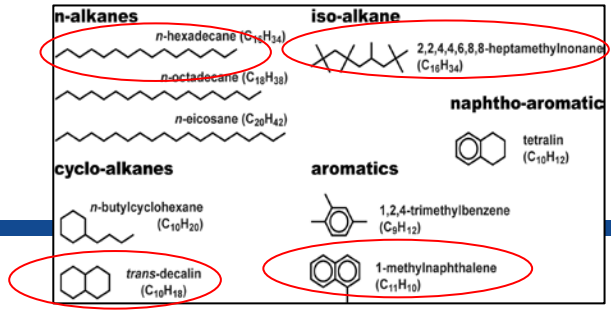






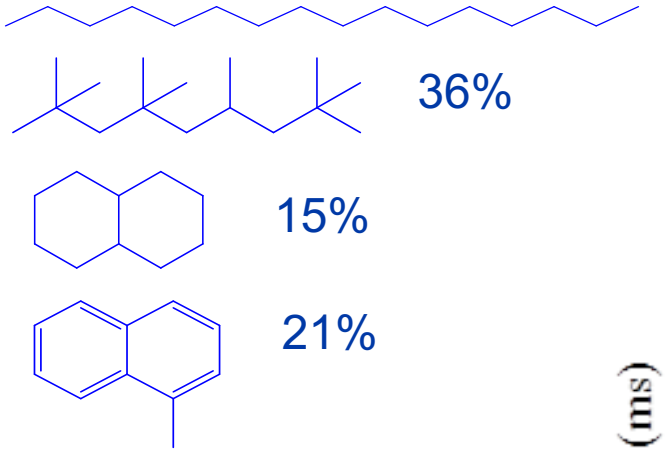
Wang et al, Combust. Flame, 157 (2010), 1976-1988

Predictions from 9-component diesel surrogate model compare well with RCM ignition delay measurements of CRC V0a*



CRC AVFL-18 9-component diesel surrogate

CRC V0a surrogate composition (Mole %):

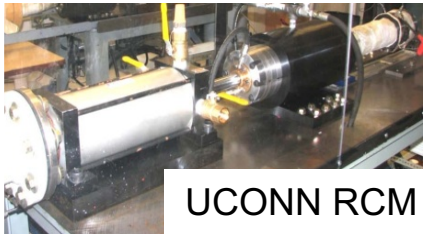


28%

36%

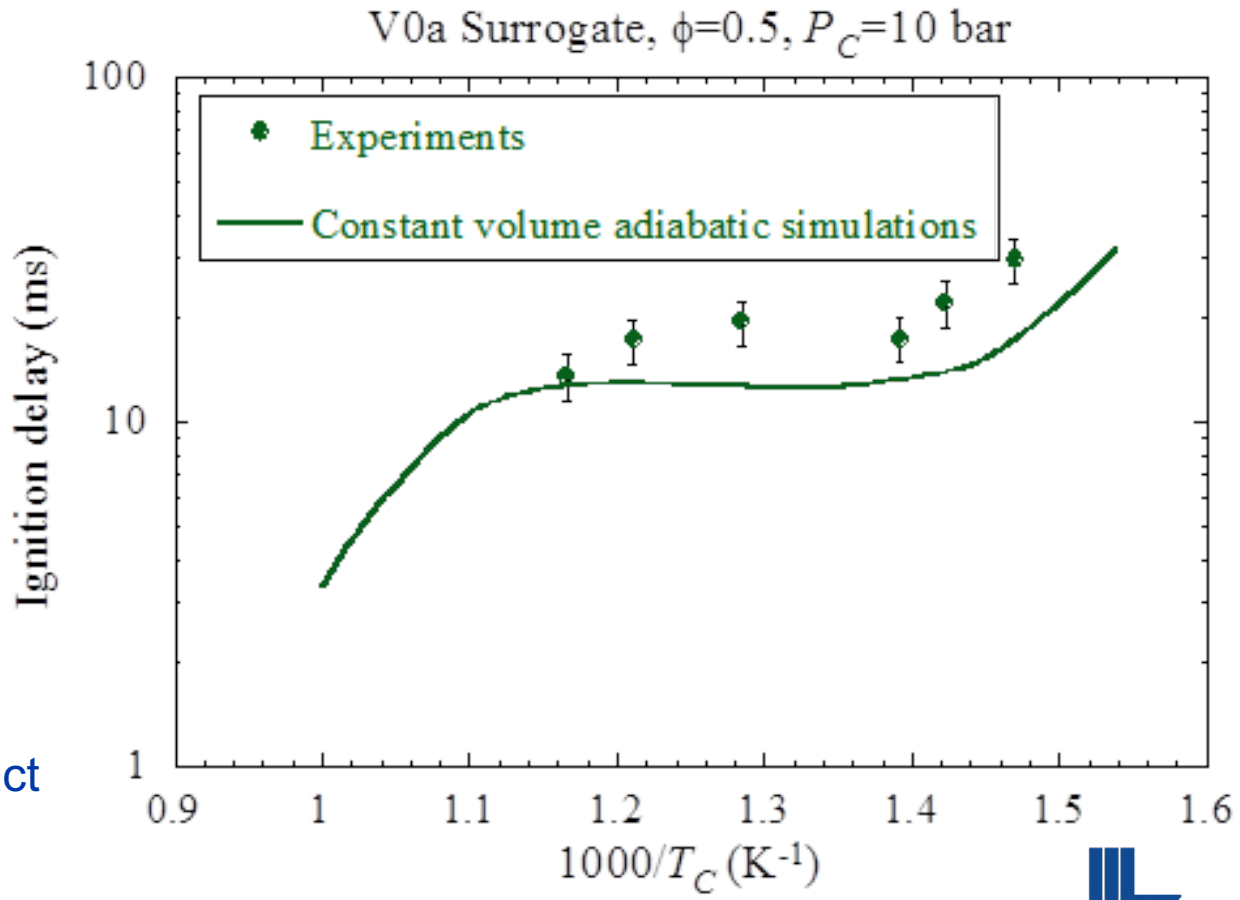
15%

21%



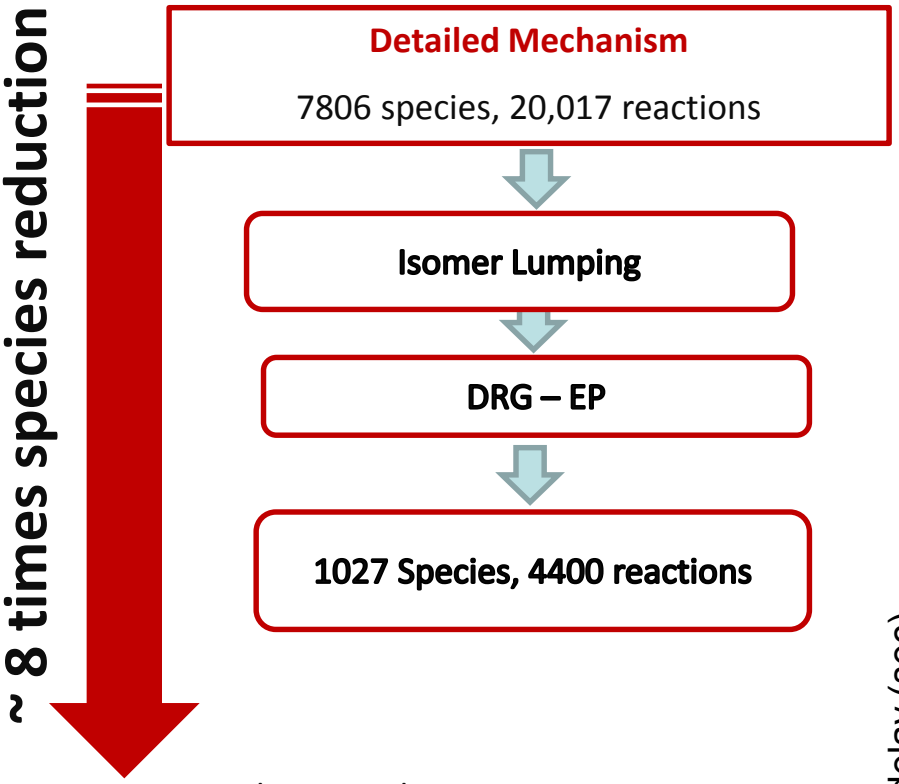
UCONN RCM

Experimental data from UCONN through subcontract



(* CRC AVFL-18a)

CRC AVFL-18a V0a mechanism reduction for ANL 3-D simulations of diesel spray combustion



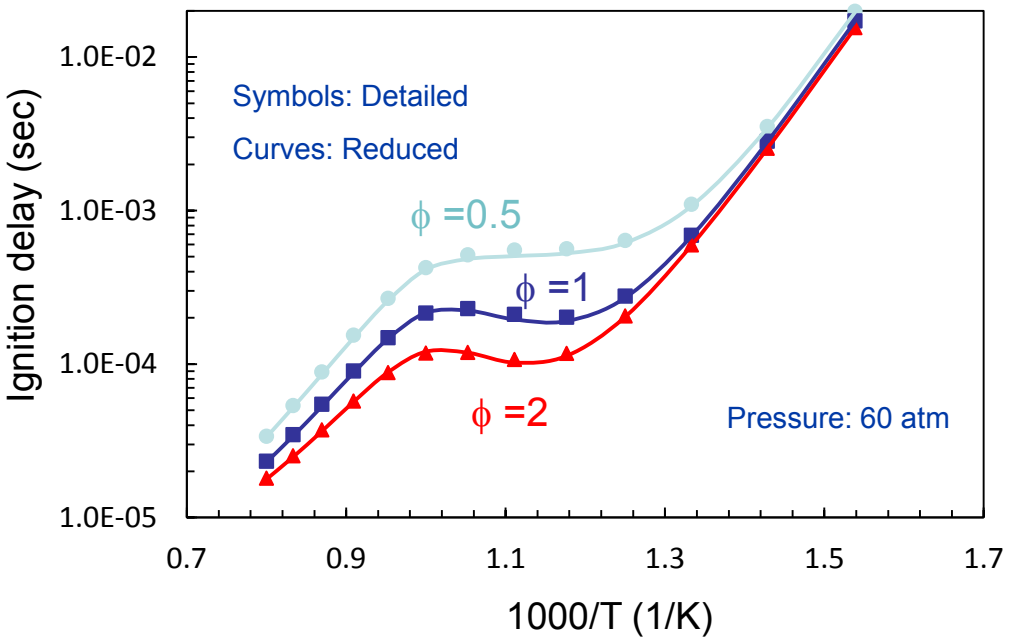
Computational time scales:

- with N^2 ~ N^3 of number of species
- Linearly with number of reactions

Range of operation:

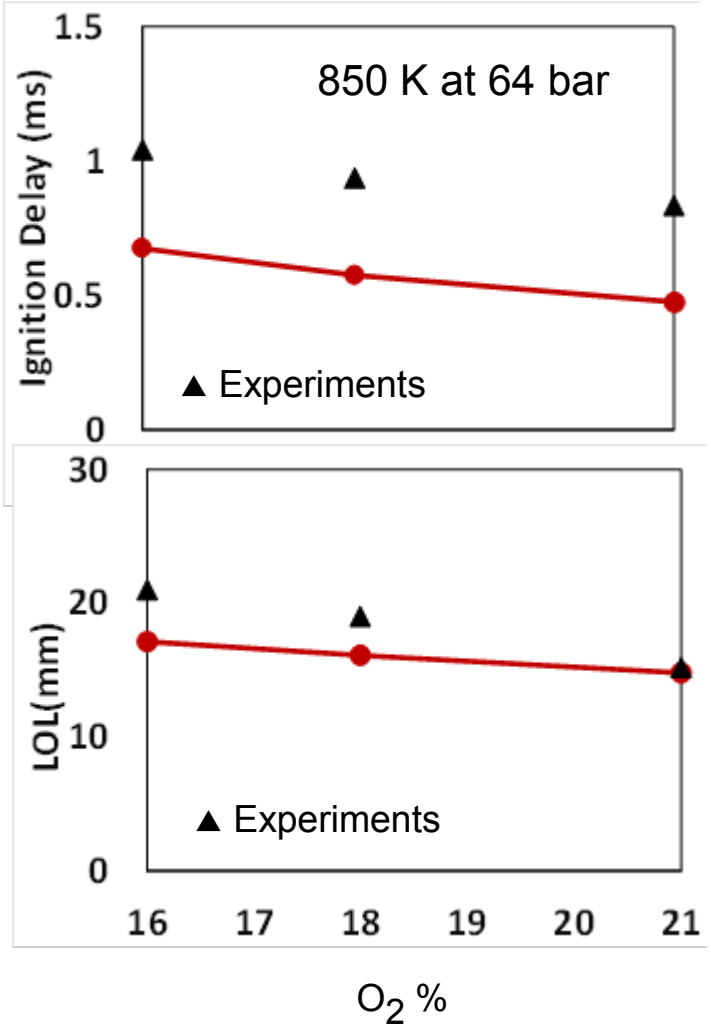
- ✓ Pressure: 10-100 atm
- ✓ Equivalence ratio: 0.5-2.0
- ✓ Initial temperature: 600 – 1300 K

- V0A surrogate mechanism was reduced for use in Tabulated Flamelet Model (TFM) for 3D spray flame simulations by ANL
- ~1000 species mechanism 3D CFD simulations are unprecedented and will offer more insights into the combustion process compared to ~100 species mechanisms that are typically being used for diesel surrogates

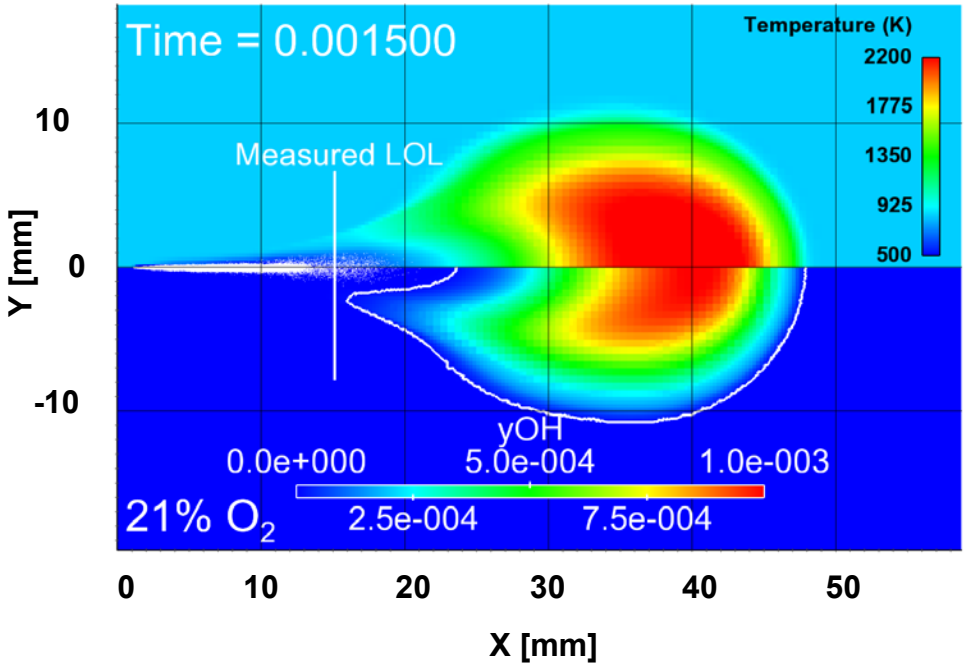


TFM model from ANL used with V0a* mechanism to simulate ARL constant-volume combustion-chamber spray measurements

ARL constant volume combustion measurements



Tabulated Flamelet Model (TFM) calculations: Kundu and Som, ANL:

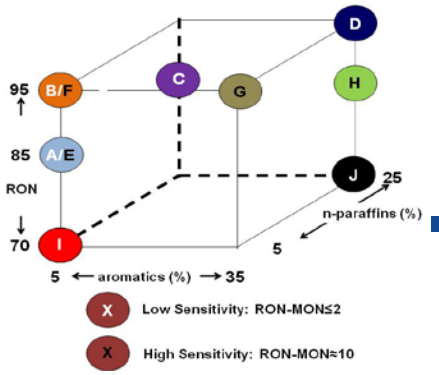


Experimental data from ARL (M. Kweon, J. Temme, and V. Coburn)

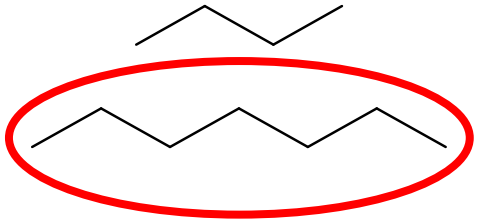
(* CRC AVFL-18a)

Improving gasoline surrogate models:

Fuel component mechanisms in 10-component gasoline surrogate palette are being improved and validated

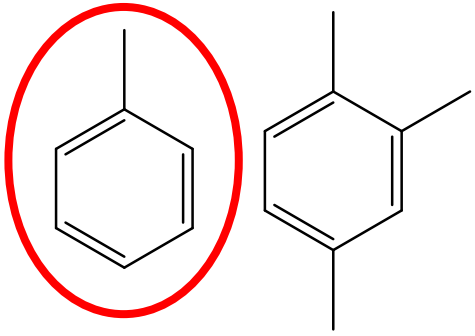


n-alkanes



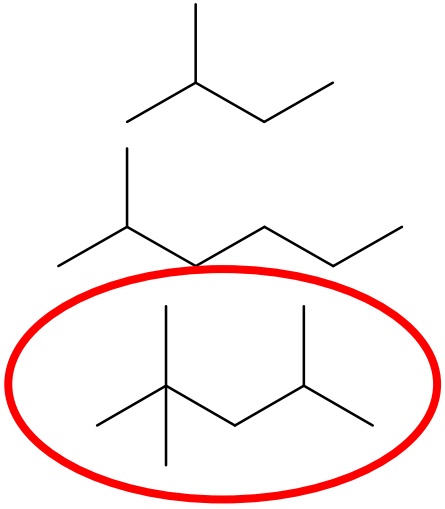
Allow to match the average chain length

aromatics



To match the molecular weight and the degree of alkyl substitution

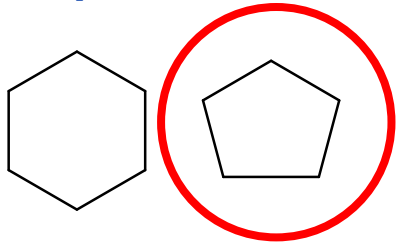
iso-alkanes



To match the average molecular weight and the degree of branching

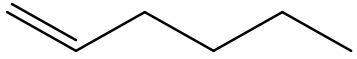
Improved

naphthenes



Two representative species

olefins



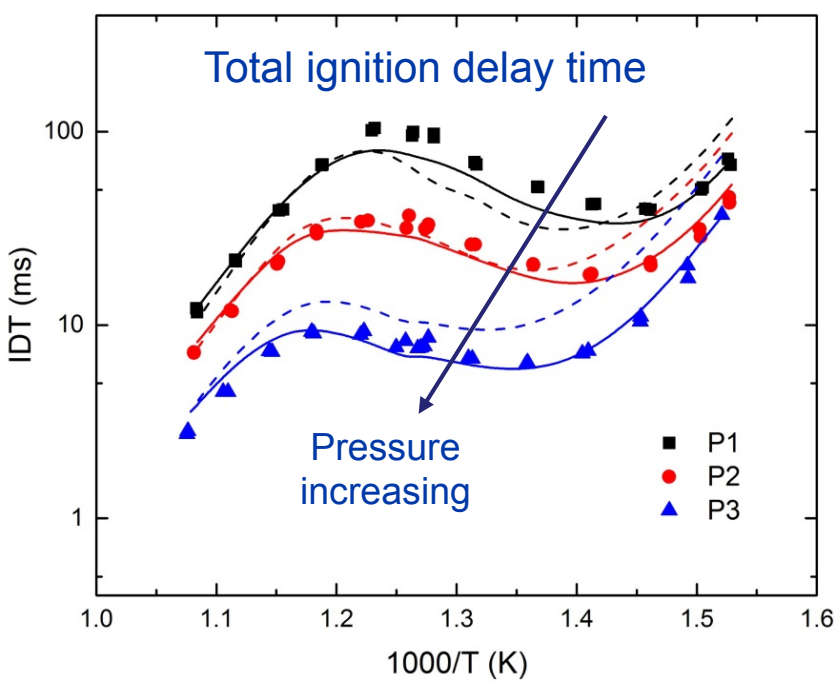
Major unsaturated linear species

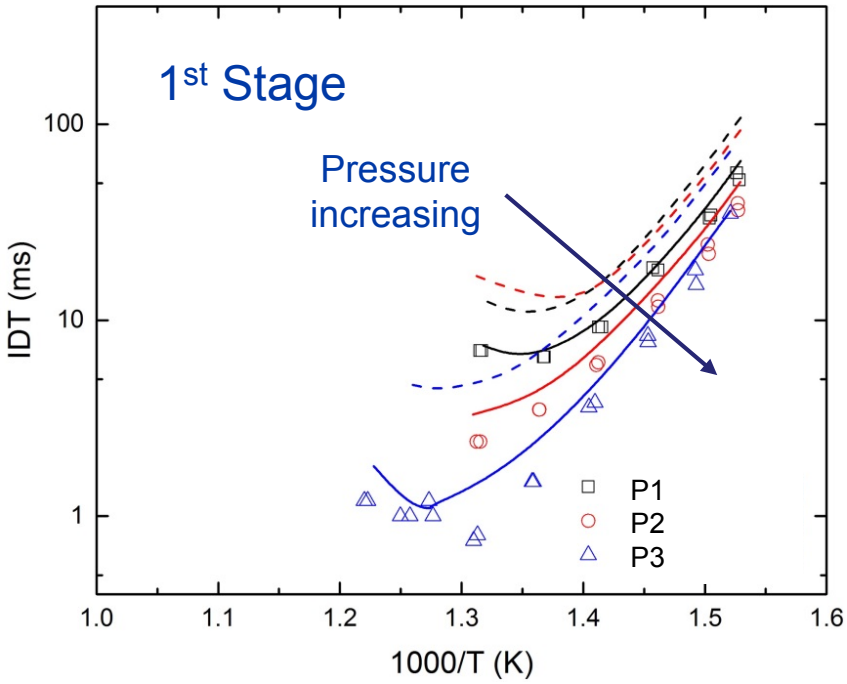
Collaborative work with ANL, NUI-Galway, KAUST, and UCONN

iso-Octane sub-mechanism improved

- Improved pressure dependence
- Improved first stage ignition (low temperature fuel chemistry)

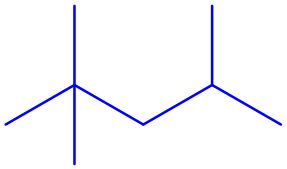
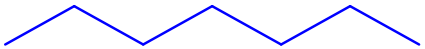
Experimental data from ANL RCM (Phi = 1.0 in air)



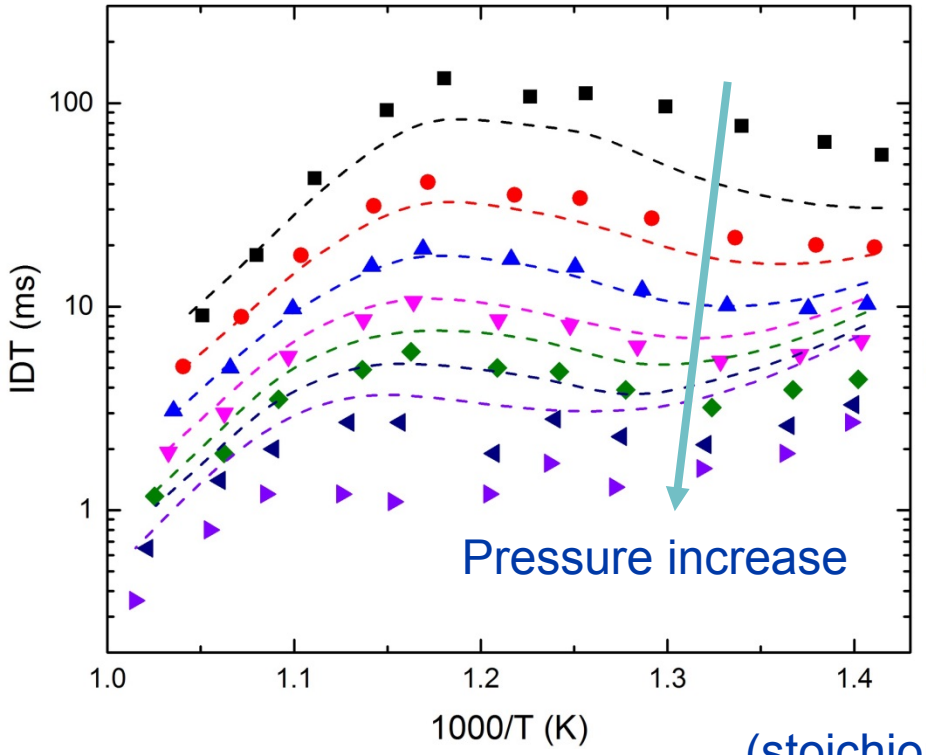


Improved mechanism
Previous mechanism

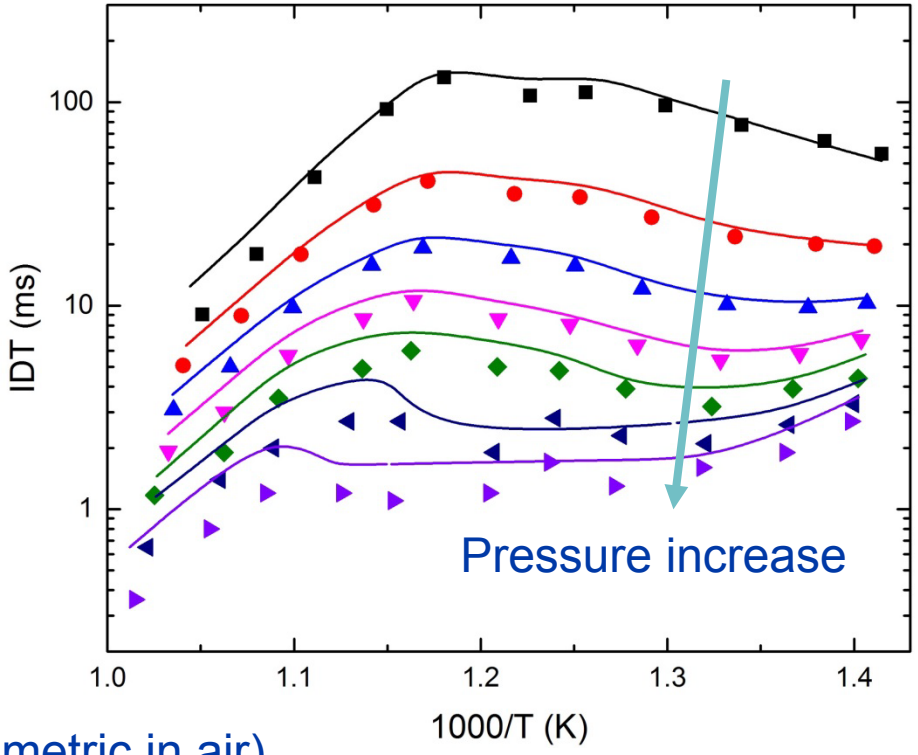
Updated PRF kinetic model better simulates pressure dependence in ANL RCM experiments

PRF90: 90 %  + 10 % 

Previous



Updated



(stoichiometric in air)

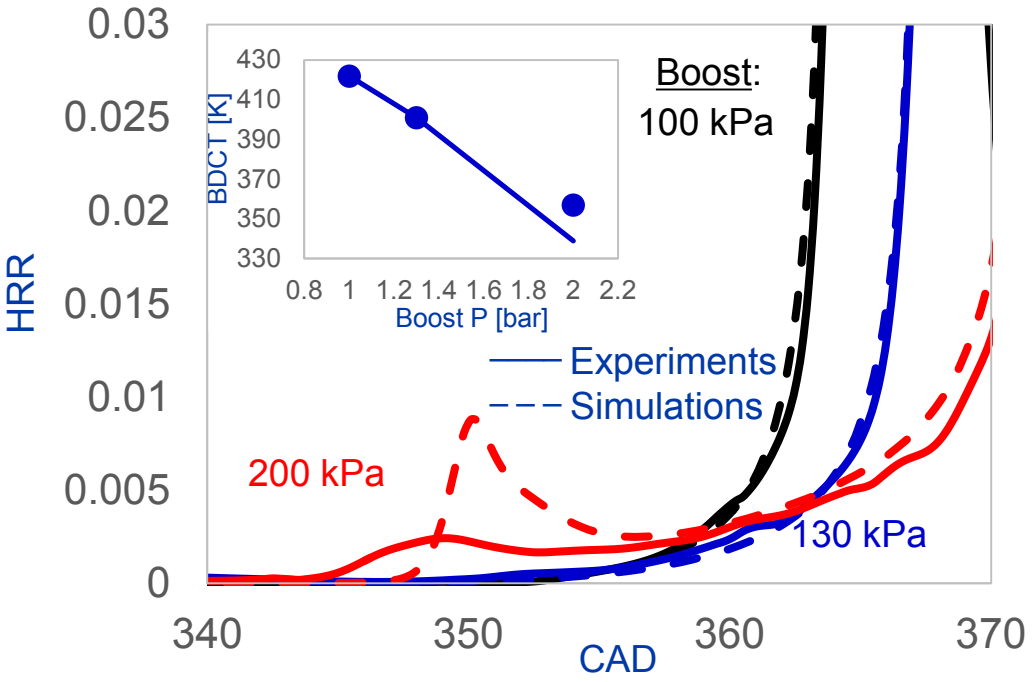
Experimental data: Goldsborough et al. ANL RCM

Simulated heat release rate (HRR) curves compare well with boosted HCCI engine experiments for E10 gasoline

5-component gasoline surrogate has been proposed by LLNL to simulate the ignition behavior of reference RD5-87 gasoline (E10 and 87 AKI):

Mole %

Class	RD5-87	Surrogate
Paraffins	16.3%	15.0%
Iso-paraffins	23.6%	35.0%
Naphthenes	12.2%	-
Aromatics	21.1%	23.0%
Olefins	5.8%	6.0%
Ethanol	19.9%	21.0%



Experiments: Dec and Dernotte, SNL

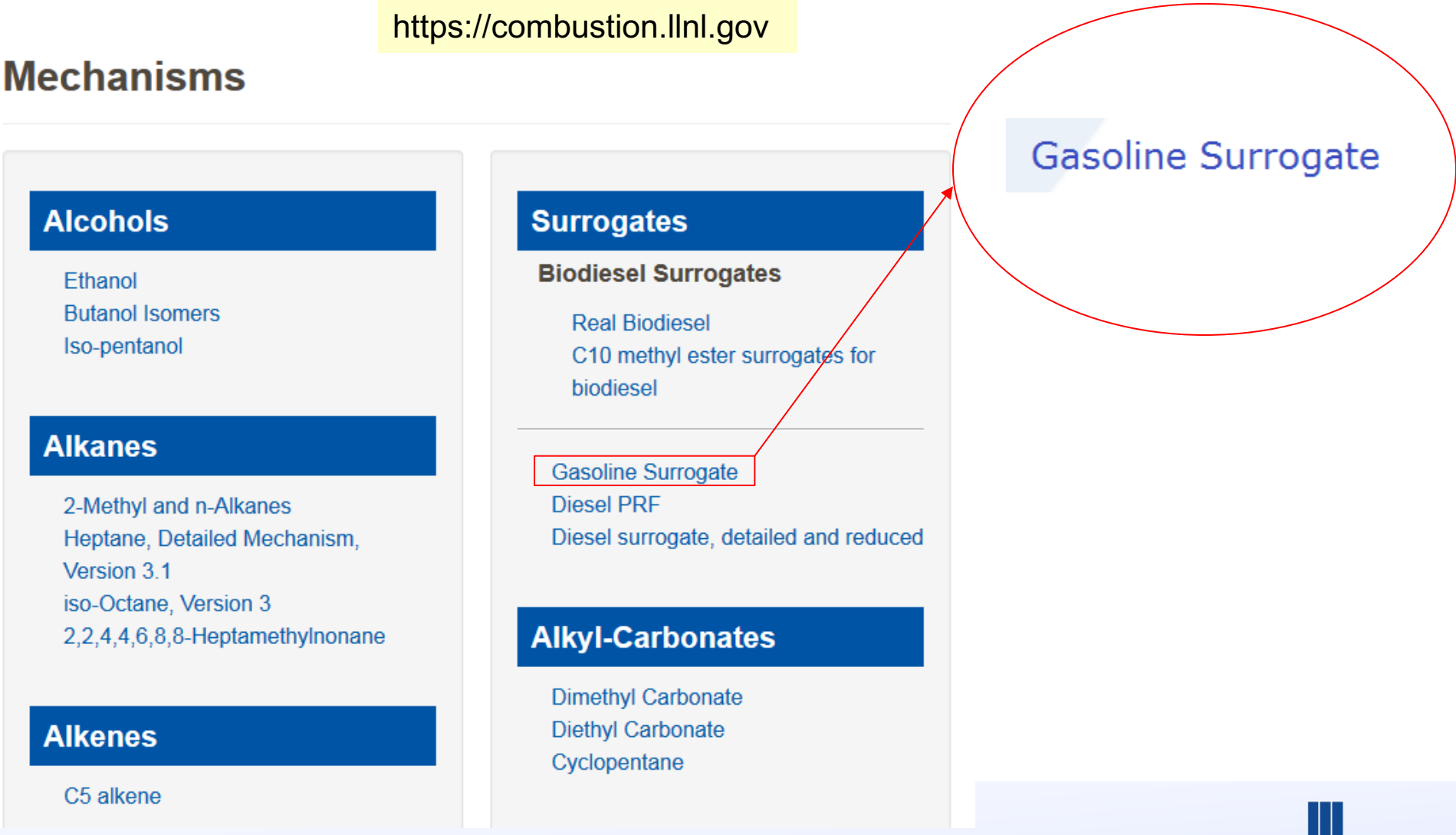
Simulations: Cernansky, Mehl, Pitz

BDC temperature was varied to match the CA50 of the simulations with the CA10 of the experiments (simulating the conditions of the adiabatic core)

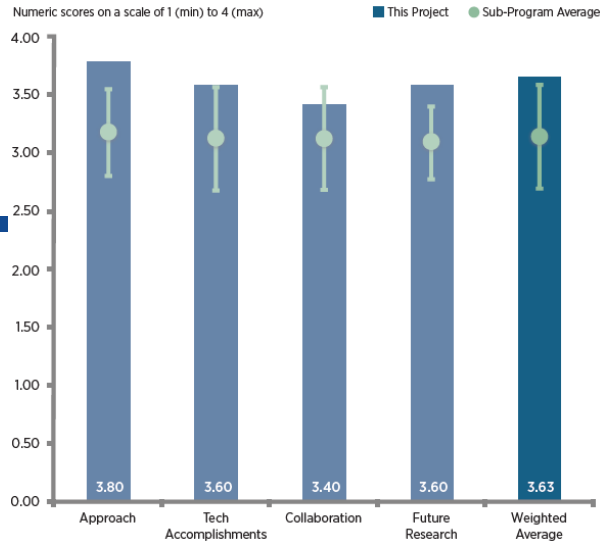
The simulated HRR profiles are found to be consistent with the experimental ones exhibiting the onset of a LTHR event rapidly degenerating into ITHR. Strong sensitivity to the surrogate composition was observed.

Mechanisms are available on LLNL website and by email

https://combustion.llnl.gov



FY2016 Reviewer's comments and our responses



Chemical Kinetic Models for Advanced Engine Combustion: Bill Pitz (Lawrence Livermore National Laboratory) - ace013

Presenter
Bill Pitz, Lawrence Livermore National Laboratory

Overall, the reviewer's comments were very positive

- The reviewer commented: "Work on gasoline should continue to be accelerated, including the effect of EGR and more equivalence ratios, pressures, and temperatures. The development of improved surrogate mechanisms for high-octane gasoline fuels and gasoline fuels with ethanol is a very critical need."
- Response: "ANL is conducting RCM experiments with a high-octane FACE fuel F with various amounts of ethanol that will be used to improve the gasoline surrogate mechanism."
- The reviewer commented: "The researchers elaborate on the availability of the reaction mechanisms to the broader engine modeling community."
- Response: "Our mechanisms are available to OEMs in the DOE AEC working group prior to publication. When published, we post our mechanisms on the LLNL website."
- The reviewer commented: "While the PI has close interactions with other institutions, it would be really nice to show results of such collaborations... for practical engine combustion simulations."
- Response: "This talk showed how diesel surrogate mechanism was reduced and used in simulations of a reacting diesel spray."

Collaborations

- Our major current industry collaboration is via the DOE working group on Advanced Engine Combustion
  - All results presented at Advanced Engine Combustion Working group meetings (Industry, National labs, Universities)
  - Multiple exchanges of chemical kinetic models with industry
  - Collaboration on gasoline/gasoline-ethanol engine experiments with Sandia:
    - John Dec on HCCI and Magnus Sjöberg on DISI
  - Collaboration at ANL with Sibendu Som on diesel reacting sprays and Scott Goldsborough on RCM experiments
- Second interaction is collaboration with many universities
  - Prof. Sung's group, U of Conn., and Dr. Sarathy, KAUST
  - Dr. Curran at Nat'l Univ. of Ireland on gasoline and diesel fuel components in RCM and shock tube
- Participation in other working groups with industrial representation
  - CRC Fuels for Advanced Combustion Engines (FACE) Working group and CRC AVFL-18a (Improved diesel surrogate fuels for engine testing and kinetic modeling)

Remaining Challenges and Barriers

- Develop chemical kinetic mechanisms for surrogates for diesel and gasoline fuels that are predictive at high pressures and with EGR found in advanced engine combustion regimes
- Improve accuracy of chemical kinetic mechanisms so that desired predictability needed by engine designers can be achieved
- Develop predictive models for diesel surrogates, particularly new versions of diesel surrogates from CRC AVFL-18a that have more representative palette compounds
- More accurately simulate the fuel effects with changing EGR, equivalence ratio and fuel composition
- Validate chemical models for blends using shock tube and RCM experimental data

Future work

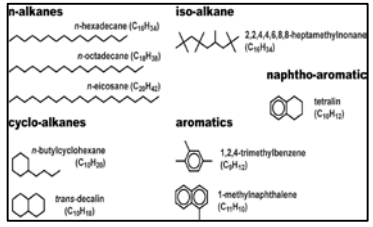
- Validate and improve our new chemical kinetic model for diesel surrogate fuels with new experimental data on target CRC diesel fuels and surrogate fuels from UCONN rapid compression machine, Army Research Lab and SNL constant-volume combustion spray chamber, and Sandia optical-access diesel engine
- Develop sectional soot kinetic model and incorporate it into the diesel surrogate mechanism so that soot emissions can predicted
- Validate and improve gasoline surrogate kinetic model over a wide range of pressures and temperatures using new experimental data on gasoline surrogates from ANL
- Work with CFD modelers to provide reduced versions of diesel surrogates to simulate diesel engine combustion
- Improve gasoline surrogate component models with new shock tube and RCM data from NUIG on octane isomers

(Any proposed future work is subject to change based on funding levels)

Detailed chemical kinetic modeling summary

Developing fuel surrogate models for gasoline and diesel fuels to enable accurate advanced engine combustion simulations with fuel effects

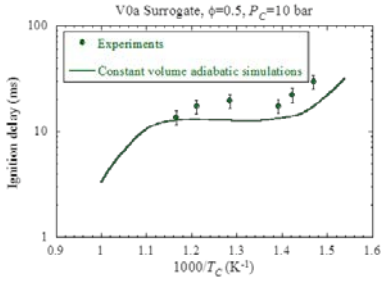
1. Assembled and tested chemical kinetic model for the 9-component CRC AVFL-18 diesel surrogate palette



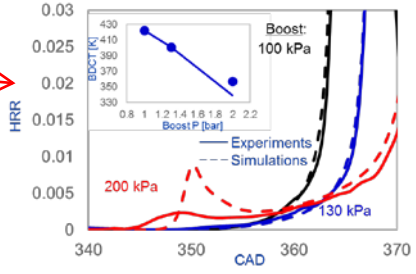
CRC AVFL-18 9-component diesel surrogate

2. Gasoline and diesel surrogate component models and binary-blend models improved

3. Diesel surrogate model tested against UCONN RCM data for CRC V0a 4-component diesel surrogate



4. Gasoline surrogate model tested against SNL HCCI engine HRR data for RD5-87 E10 gasoline

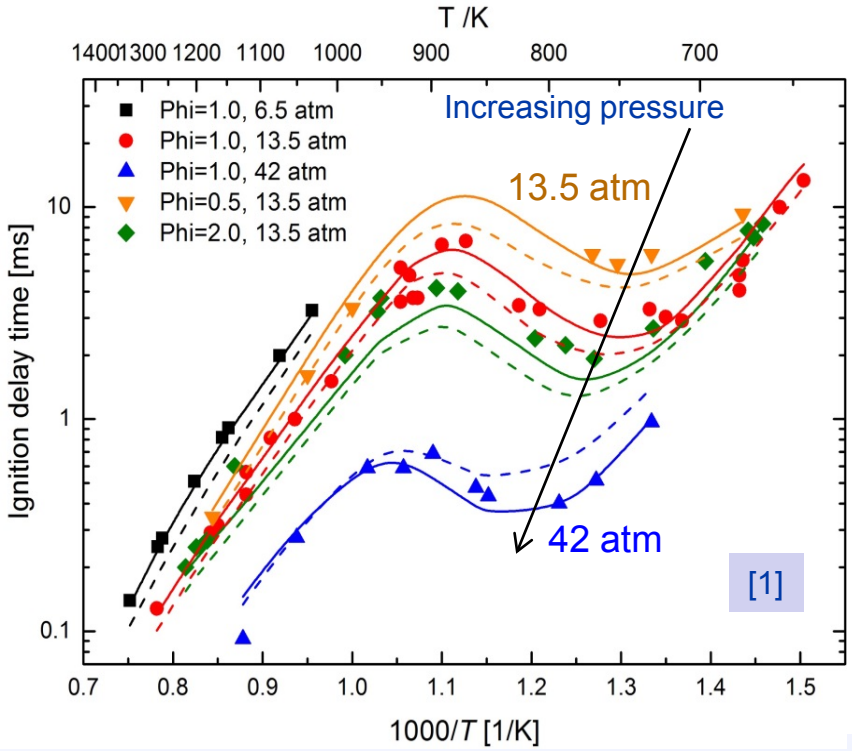


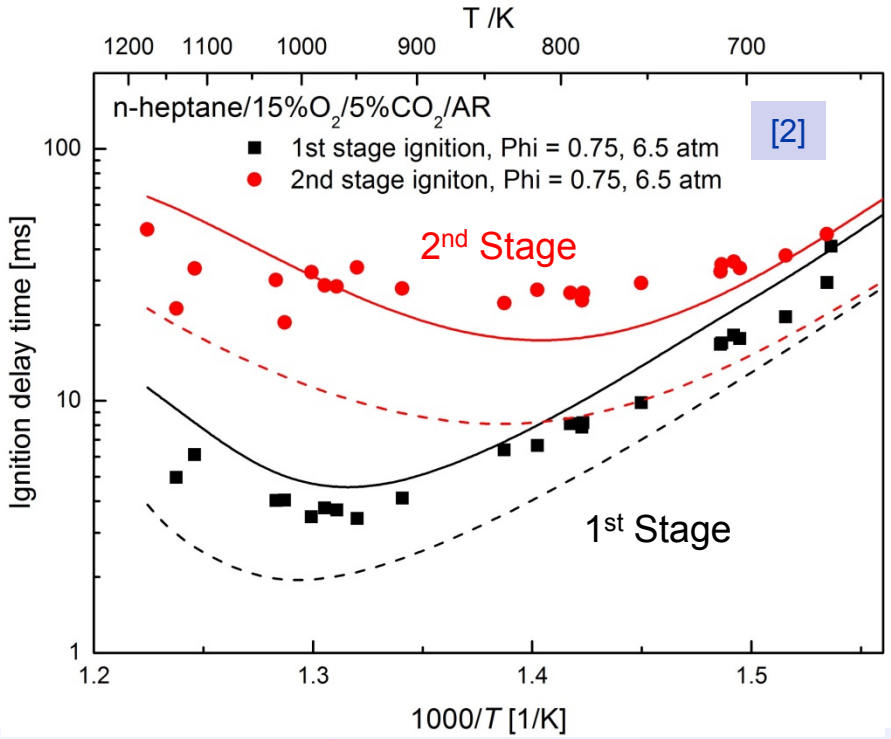
5. Diesel surrogate model reduced and compared to constant volume combustion spray data using TFM code in collaboration with ANL and ARL

Technical Back-Up Slides

Improved n-heptane sub-mechanism (work at NUIG)

- K Zhang et al., Combustion and Flame 172, 116-135
  - Better predicted pressure dependence (base chemistry)
  - Better predicted first stage ignition (low temperature fuel

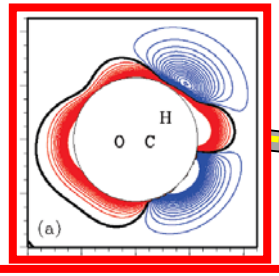




Solid line: Improved mechanism
Dashed line: Previous mechanism

[1] H. Ciezki and G. Adomeit, Combust. Flame, 93, (1993) 421-433
[2] M. F. Campbell et al., Proc. Combust. Inst., 35, (2015) 231-239

Chemical kinetic model development for practical fuels:



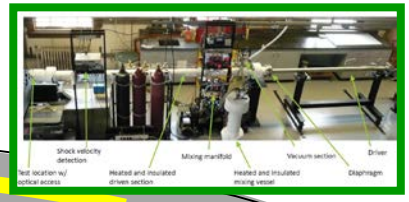
Ab initio calculations

Accurate reaction rates

Species thermodynamic properties

Reaction paths

Reaction rate rules



Detailed Chemical Kinetic Models

Fundamental Experiments

NUIG, UCONN, KAUST, USC, CNRS, RPI

Application to engines

Model Reduction

Validation against fundamental combustion data

Fast Solvers

LLNL - Numerics

Fuel component and surrogate models validated and improved by comparison to fundamental experimental data

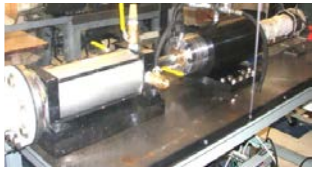
Jet Stirred Reactors

Premixed Laminar Flames

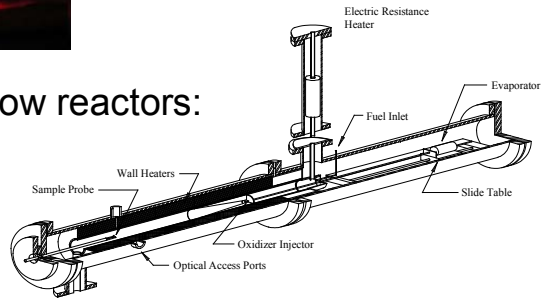
Shock tube

Non Premixed Flames

Rapid Compression Machine



High pressure flow reactors:



Engine Combustion

<u>Combustion Parameters</u>

Temperature

Pressure

Mixture fraction (air-fuel ratio)

Mixing of fuel and air